On Refinement of Several Physical Notions and Solution of the Problem of Fluids for Supercritical States

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Abstract

To solve the ancient problem of fluids, i.e., of states in which there is no difference between gas and liquid (the so-called supercritical states), it is necessary to abandon several "rules of the game", which are customary to physicists and to refine them by using rigorous mathematical theorems.

To the memory of V. L. Ginzburg

1 Introduction

Physicists and mathematicians have different language and different logics. Namely, a mathematician first formulates the conditions, then the theorem (the formula), and only after this proves it. A physicist, conversely, first derives a formula, which he makes rather convincingly, but he often conceals the conditions assuming them to be obvious. As a rule, mathematicians prove theorems, which have already been "known" to physicists in the sense that the physicists have been using them explicitly or implicitly for a long time.

There is a series of rather well-known theorems bearing the names of their authors, which were formulated in a different language and, in fact, had been already proved by the physicists[1]. The results of mathematicians who are translators to the mathematical language were especially easily and rapidly understood by the mathematical community.

Sometimes, a mathematician, who also obtained new results in physics and, in addition, tried to explain them in the physical language, was not taken as a mathematician by the mathematical community, and he had to prove this separately.

The author also happened to obtain several results concerning the area of interests of those who doubted[2], see [1], [2], and the work [3] continued in [4] (how Levsha had to "show a flea"), in order to make the mathematical community to acknowledge him.

Similarly, it is difficult to make the physicists to believe that the mathematicians, who follow rigorous logics, can obtain results that are paradoxical from the point of view of customary understanding. Physicists are not convinced even by the fact that the mathematical results correspond to well-known experiments and predict new experiments, which are in a rather good agreement with the theoretical calculations. One of my friends, a famous physicist, used to tell me: "You do not convince me by your lemmas".

In the second part of the famous book of Feynman and Hibbs about continual integrals, the unrigorous logics of Feynman continuous integrals (which was useful for physicists)

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[1]Proved in the sense that neither a rigid statement nor a rigid proof required any efforts.

[2]That the author is a rigorous mathematician and it is impossible to find errors in his works.

led to the rigorous results obtained by Norman Wiener twenty years ago (no reference was made).

The author had to "prove" the semiclassical asymptotics of the Feynman continuous integrals (he proved it indirectly somewhat earlier) according to the Feynman logics (V. Guillemin and S. Sternberg repeated the proof in [5], but fairly quoted the word "proof").

The "rules of the game" developed by physicists are very useful, because they allow them to "jump over" the mathematical difficulties and hence to proceed significantly faster. Their physical intuition developed in experiments in different areas of physics helps them to feel the result empirically, especially if the numerical data are known. The latter allows them to avoid complicated asymptotics in several small parameters and a nonstandard analysis. In the first aspect (the intuition), I was always surprised by B. L. Ginzburg; in the second aspect (the knowledge of numerical data), by Ya. B. Zeldovich, who, even speaking over phone, could mentally calculate whether or not a given theorem corresponds to physics.

If a mathematician does not have any physical intuition (for example, just as the author[3]), then he can be severely disappointed considering some well-known physical law as an axiom and obtaining an answer contradicting the experimental data. Therefore, prior to presenting mathematically rigorous results, which correspond to the unsolved problems of chemistry (and even of alchemy, because the term "fluids" was introduced by alchemists[4]), we show that some well-known, even "eternal" physical and mathematical "verities" turn out to be significantly refined in the case of rigorous mathematical verification.

Remark 1. To distinguish the classical theory in its modern understanding from the quantum theory, it is necessary somewhat to change the physicist's ideology that the classical theory is the theory that existed in the 19th century before the appearance of the quantum theory. But, in fact, the classical theory is the theory obtained from the quantum theory in the limit as $h \to 0$.

So Feynman was right stating that spin is a phenomenon of classical mechanics. Indeed, this is the case in rigorous passing to the limit from quantum to classical mechanics. Similarly, the ray polarization does not disappear as the frequency increases and hence is a property of geometric rather than wave optics, as was used to think because the light polarization was discovered as a result of discovering the wave optics.

We consider the "Lifshits well", i.e., the one-dimensional Schrödinger equation with potential symmetric with respect to the origin and having two wells. Its eigenfunctions are symmetric or antisymmetric with respect to the origin. As $h \to 0$, this symmetry remains unchanged, and since the squared modulus of the eigenfunction corresponds to the probability that a particle stays in the wells, it follows that, in the limit as $h \to 0$, i.e., "in the classics", for energies less than the barrier height, the particle occurs between the wells, in the two wells at once, although the classical particle cannot penetrate through the barrier. Nevertheless, this simple example shows the variation in the ideology of the "classical theory".

To understand this paradox, it is necessary to take into account that the symmetry must be very precise and the state stationarity means that this state appears in the limit

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[3]In particular, my model of the Chernobyl pile-up cooling turned out to be erroneous (see [44]).

[4]The alchemists were not far from truth, for example, addition of 1% of methanol to a carbon dioxide fluid results in that CO_2 on the critical isotherm behaves as the 100% methanol in several extraction processes. In technology, the supercritical water vapor is used in turbines in all thermal and nuclear power stations.

of "infinitely large" time. As we show below, the same concerns the Bose-distribution in the classical theory of gases.

Now we show how the existence of an additional parameter changes the representation in the classical limit. We dwell upon the notion, which is called "collective oscillations" in classical physics and "quaseparticles" in quantum physics. In classical physics, this is the Vlasov equation of self-consistent (or mean) field, and in quantum physics, this is the Hartree (or Hartree–Fock) equation.

So we want to note the following point that seems to be paradoxical. The solutions of the equation in variations for the Vlasov equation *do not coincide* with the classical limit for the equations in variations for the mean-field equation in the quantum theory. This is because of the fact that the variations are related to another small parameter, namely, the variation parameter. And this is already the field of nonstandard analysis.

N. N. Bogolyubov, for example, in [6], studied the problem without an external field, and the asymptotics thus obtained coincides with the semiclassical asymptotics in an external field [7], [8]. Moreover, this is in fact the classical limit, because the parameter h^2 in this Bogolyubov's paper can be compensated by a large parameter, namely, the wave number k. This becomes especially obvious if the interaction is assumed to be zero. Then an ideal gas is obtained, which in this case can be considered as a classical gas. Just therefore, the author proved that the classical fluids in nanotubes have superfluidity (see [11], [12]), which was confirmed by a series of experiments (see the references in [11]).

Confusion is due to the fact that the constant h has dimension of action, and, rather often, in the classical limit, in order to keep the dimensions, it participates even in the Maxwell distribution [13]. For example, the Thomas–Fermi equations (including the temperature equations) are classical equations from the above point of view, but the fact that they contain the constant h leads to confusion. Therefore, the Van der Waals law of corresponding states is very important, it allows us to consider the reduced temperatures $T_r = T/T_{cr}$ and pressures $P_r = P/P_{cr}$ as dimensionless quantities.

Remark 2. Now we consider the N-particle Gibbs distribution

$$\mathcal{P} = e^{-\frac{H(q,p)}{kT}}, \qquad H(q,p) = \frac{p^2}{2m} + U(q), \qquad q \in R^{3N}, \qquad p \in R^{3N} \qquad (1)$$

where $H(q,p)$ is the Hamiltonian. It is assumed that the level surfaces $H(p,q) = \mathrm{const}$ are simply connected.

The theorem about this distribution was in fact proved in [14]. It must be considered in the sense of Kolmogorov complexity. This distribution is the distribution over the number of different experiments whose number L is independent of N, over systems of N particles at the same temperature (the average distribution over the number of experiments), and it is the distribution over the energy surfaces $H(p,q) = \mathrm{const}$, $p \in R^{3N}$, $q \in R^{3N}$:

$$E_1 \leq H(p,q) \leq E_2,$$

where E_1 and E_2 are less than some average energy E, $\Delta E = E_1 - E_2 \ll E$, and the phase volume is $\Delta \omega = \int dp\, dq$, $E_1 \leq H(p,q) \leq E_2$.

We divide the phase space $(p,q) \in R^{6N}$ into finitely many domains

$$E_l \leq H(p,q) \leq E_{l+1}, \qquad (2)$$

where $l = 0, \ldots, s-1$, $E_0 = 0$, $E_s = E$, $p \in R^{3N}$, $q \in R^{3N}$, and, correspondingly, the phase space R^{2NL} has coordinates $p_1, q_1, p_2, q_2, \ldots, p_N, q_N$. We perform ordered sampling

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with return L_l from the partition of domains in the space R^{2NL} into the "box" $E_l \leq H(p,q) \leq E_{l+1}$, under the condition that

$$\sum_{i=1}^{L} \frac{1}{\Delta\omega} \int_{L_i \leq H(p,q) \leq L_{i+1}} H(p,q)\, dp\, dq. \tag{3}$$

From the physical viewpoint, the ordered sampling means that L distinguishable $3N$-dimensional particles are considered. Let $\rho_{E_l}^{\Delta}$ be the number of $3N$-dimensional "particles" in the energy interval $E_l \leq H(p,q) \leq E_{l+\Delta}$ divided by $\Delta\Omega$.

Assume that the above conditions on the function $H(p,q)$ are satisfied. We determined L from the condition[5]

$$\frac{1}{\Delta\omega} \int_0^\infty e^{-bH(p,q)}\, dp\, dq = L \qquad b = \frac{1}{kT}, \qquad p, q \in R^{6N}, \tag{4}$$

where k is the Boltzmann constant. We determine E in (3) as $\int_0^\infty H(p,q)e^{-bH(p,q)}\, dp\, dq$. Then we have the following theorem.

Theorem 1. The following relation holds:

$$\mathcal{P}\left(\left| L\rho_{E_l}^{\Delta} - \frac{1}{\Delta\omega} \int_{E_l \leq H(p,q) \leq E_{l+1}} e^{-bH(p,q)}\, dp\, dq \right| \geq \sqrt{L \ln L} \right) \leq L^{-m}, \tag{5}$$

where m is arbitrarily integer.

Here the probability $\mathcal{P}$ is the Lebesgue measure of the phase volume in parentheses in (5) with respect to the entire phase volume R^{6NL} bounded by (3).

Thus, the Gibbs distribution is not a distribution over momenta and coordinates, but is a distribution over the energy levels.

If the domain (2) is multiply connected, then the problem can be solved only by semiclassical transitions. If $N = 1$, then we formally obtain the Maxwell–Boltzmann distribution. But the latter is considered, as a rule, as the average distribution for N particles. We discuss this treatment in Remark 5.

Boltzmann obtained his distribution integrating this distribution over p. But this can be done under the following conditions only.

For a great many particles, their dependence on a common potential field must be assumed to be slowly varying as a rule. Indeed, if the particles are in a volume V (or in an area S), then the thermodynamical asymptotics requires that the volume V (the area S) tend to infinity. But this means that the potential field varies very slowly, and it must be assumed that the function of the coordinates is of the form

$$H\left(p, \frac{q}{\sqrt[3]{V}}\right).$$

Otherwise, we have no rights to pass from the Gibbs distribution from the Maxwell–Boltzmann distribution $e^{-\beta(p^2+U(q))}$ (integrating it over the momenta) to the Boltzmann distribution of the form

$$e^{-\beta U(x)}, \tag{6}$$

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[5]If the temperature kT is considered as average over the the number of particles, then $b = \frac{1}{kNT}$. Here kNT is the average energy over the number of experiments.

since the Maxwell–Boltzmann distribution is not a distribution of the density of the number of particles with respect to the momenta and coordinates. This distribution can give only the number of particles between energy levels of the form

$$\frac{p^2}{2m} + U(x) = \text{const.}$$

But if $U(q)$ is of the form

$$U(q) = F(\frac{q}{\sqrt[3]{V}}),$$

then this integration can be done in the thermodynamical asymptotics as $V \to \infty$.

One should not forget here that the Boltzmann distribution is also far from being a distribution with respect to the coordinates q, and that it is a distribution with respect to level surfaces of the function $U(q)$ only.

Remark 3. There is a mathematical error in the very definition of thermodynamical limit as the limit as $N \to \infty$ and $V \to \infty$ such that $N/V = \rho$, where ρ (the density) is finite.

Let the pressure be $P \sim 1/23$ atm. This pressure does not lead to a too rarified gas (and is admitted by the Knudsen criterion).

Obviously, the above definition is incorrect because the number of particles is bounded by Avogadro's number. As $N \to \infty$, we have $\ln N \to \infty$ as well. But $\ln N \sim 23$ and $\ln N$ is not large under the above pressure. It would be correct to pose the problem, as was said above, neglecting the inverse quantity $(\ln^2 N)^{-1}$. In this case, a mathematically rigorous asymptotics in statistical physics would be obtained.

Remark 4. The transfer of the Bose distribution for photons to gas in the form of the Bose–Einstein distribution is incorrect. Since $\sum N_i = N$, where N_i stands for the number of particles at the energy level ε_i, cannot vary up to infinity ($N_i \leq N$), it follows that the chemical potential μ can take positive values, which must not be neglected [15]. This restriction means that parastatistics must be considered.

Remark 5. The most essential is the note that the distribution given in Remark 4 with the property that N and $\ln N$ are finite permits preserving the parastatistics of the Bose–Einstein-type distribution as $h \to 0$, and just this property will be used in what follows. The fact that it holds in the classical limit is especially unusual for the physicists (cf. Remark 1.).

Therefore, in addition to references to exact theorems, I also present several other arguments. For example, the physicists completely accepted the financial considerations presented in [16].

"A general important property of money bills is that the change of one money bill by another of the same denomination does not play any role. This property, which can be called "money do not smell", permits uniquely determining the formula for nonlinear addition. We assume that we want to deposit two copecks into two equivalent banks. How many possibilities do we have? We can deposit both copecks into the first bank, or deposit both copecks into the second bank, or deposit per one copeck in each of the banks. Thus, we have three possibilities. But if we want to deposit two diamonds, then we have four possibilities, because we can interchange the diamonds. At the same time, it does not make any sense to interchange the copecks. The identity property of money bills of the same denomination permits changing the number of versions. This statistics, just as the statistics of identical Bose-particles is called the quantum statistics (Bose-statistics), and the statistics of diamonds (provided that they are not absolutely identical) is called

the classical statistics. But as we see, the Bose-statistics can be applied to money, more precisely, to money bills."[16], p. 5. And this is despite the fact that the copecks may have different years of their issue and the money bills have individual numbers. Objectively, they are different, but for our problems, this difference is not essential, because only the quantity of money bills is important for us.

Further, the physicists did not protest, when Schoenberg used the creation and annihilation operators in classical mechanics [10]. And this is possible only when considering the Fock space of identical particles.

We consider one more aspect of this problem in more detail, because the molecular dynamics of classical particles is nowadays commonly used.

In the well-known textbook [17] by Landau and Lifshits, the authors explain the identity principle for particles as follows: "In classical mechanics, identical particles (such as electrons) do not lose their 'identity' despite the identity of their physical properties. Namely, we can visualize the particles constituting a given physical system at some instant of time as 'numbered' and then observe the motion of each of them along its trajectory; hence, at any instant of time, the particles can be identified. ... In quantum mechanics, it is not possible, in principle, to observe each of the identical particles and thus distinguish them. We can say that, in quantum mechanics, identical particles completely lose their 'identity' " (p. 252).

There are similar explanations of the identity principle for particles in other textbooks as well.

But, as a matter of fact, if the initial data for the Cauchy problem does not possess a symmetry property, then the situation in quantum mechanics does not differ from that in classical mechanics.

Indeed, suppose that the Hamiltonian function

$$H(x_1, p_1; x_2, p_2; \ldots; x_n, p_n)$$

is symmetric with respect to permutation of (x_i, p_i) and (x_j, p_j), $i = 1, 2, \ldots, n; j = 1, 2, \ldots, n$. Let $\widehat{H} = H(x_1, \widehat{p}_1; \ldots; x_n, \widehat{p}_n)$ denote the self-adjoint operator in the space $L_2(R^{3n})$ corresponding to the Hamiltonian $H(x_1, p_1; x_2, p_2; \ldots; x_n, p_n)$ (Weyl of Jordan quantized).

Consider the corresponding Schrödinger equation

$$ih\frac{\partial \Psi(x)}{\partial t} = \widehat{H}\Psi(x), \qquad \Psi(x) \in L_2(R^{3n}), \tag{7}$$

satisfying the initial conditions

$$\Psi|_{t=0} = \Psi_1(x_1)\Psi_2(x_2)\ldots\Psi_n(x_n)\exp\frac{i}{h}\sum_{i=1}^{n}p_jx_j, \tag{8}$$

where $\Psi_i(x) \neq \Psi_j(x)$, $p_i \neq p_j$, and we can assume that $\Psi_i(x) = f(x - x^{(i)})$, where $x^{(i)} \neq x^{(j)}$, and $f(x)$ is a bell-shaped function vanishing outside a neighborhood of the point $x^{(i)}$, and the neighborhoods are small so that these functions do not intersect. Returning in time to the initial point, we can number all the bell-shaped functions.

But in the projection on the real space R^3 containing all n particles, the experimenter cannot distinguish them without taking into account the full deterministic process with respect to time from zero to the given t.

Similarly, in classical mechanics, of two point particles have intersected and the experimenter has no knowledge of their velocities (instant photo), then he also cannot distinguish

them. He must know their original velocities, i.e., use slow-motion filming. This means that he has to look into their "past".

But if the experimenter must determine which of the original particles with a prescribed velocity arrived at the given point, then he must observe the whole process, up to the point $t = 0$.

Finally, let us consider the particle identity philosophically.

In statistical calculations of the number of inhabitants in a town, the permutation between a child and an old man does not change the total number of inhabitants. Hence, from the point of view of the statistics of the given calculation, they are indistinguishable. From the point of view of the experimenters who observes the molecules of a homogeneous gas using an atomic microscope, they are indistinguishable. He counts the number of molecules (monomers) and, for example, of dimers in a given volume. Dimers constitute 7% in the total volume of gas (according to M. H. Kalos). This means that the experimenter does not distinguish individual monomers, as well as dimers, from one another and counts their separate numbers. His answer does not depend on the method of numbering the molecules.

These obvious considerations are given for the benefit of those physicists who relate the fact that quantum particles are indistinguishable with the impossibility of knowing the world. I do not intend to argue with this philosophical fact, but wish to dwell only on mathematics and statistics and distributions related to the number of objects.

Let us turn to the Boltzmann statistics, as is described in "Mathematical Encyclopedia" [19]. In his article on the Boltzmann statistics, D. Zubarev, the well-known specialist in mathematical physics and the closest disciple of N. N. Bogolyubov, writes that, in Boltzmann statistics, "particles ... are distinguishable". However, a few lines below, Zubarev states that "In the calculation of statistical weight, one takes into account the fact that the permutation of identical particles does not change the state, and hence the phase volume must be decreases by $N!$ times".

Of course, it is impossible to simultaneously take into account both remarks. But they are both needed to solve the Gibbs paradox. As I pointed out on numerous occasions, from the mathematical point of view, the Gibbs paradox is a counterexample to the Maxwell–Boltzmann distribution regarded as a statistical distribution for a gas in which the molecules cannot be turned back, but not a counterexample to a dynamical distribution [20]. As for the famous discussion between Boltzmann and some mathematicians [21], of course, if the particles of the gas are distinguishable and can be numbered, then they can also be mentally turned back and returned to a state close to their initial state, as the Poincare theorem states.

As an example we consider the last source of errors, because the computer has a finite memory. How is the number of particles related to the computer error and the computer's ability to recover their initial data?

By way of example, we consider a set of unnumbered billiard balls of unit mass and the same color.

First, consider one billiard ball and launch it from some (arbitrary) point with velocity not exceeding a certain sufficiently large value v, i.e., with energy not exceeding $v^2/2$. However, since the computer has certain accuracy, it follows that the energy of the ball will take a finite integer number, s, of values in the interval of energies $[0, v^2/2]$: $\lambda_i = iE_0$, $i = 1, \ldots, s$, where E_0 corresponds to this accuracy.

Thus, we obtain a spectrum of energy values which can be regarded as a self-adjoint diagonal matrix of order s, where $s \gg 1$. By assigning such a discrete set of energies to a ball, we obtain the wave–particle correspondence in classical mechanics, because the

resulting matrix is unitary equivalent to any operator $\widehat{L}$ with such a spectrum in a Hilbert space H.

How many balls must be launched so that the computer will be unable to determine their initial data?

The spectrum corresponding to N balls is obtained by considering the tensor product of N Hilbert spaces: $\widehat{L}_N = \widehat{L} \times \widehat{L} \times \cdots \times \widehat{L}_{(N\text{times})}$.

The eigenvalues of this operator have the form

$$\mathcal{E} = \sum_{i=1}^{s} N_i \lambda_i.$$

If we only consider the eigenvalues symmetric with respect to the permutation of the particles of this operator, which corresponds to the identity of the balls, then the eigenvalue $\mathcal{E} = \sum_{i=1}^{s} N_i \lambda_i$ is of multiplicity equal to the number of all possible variants of the solution of the problem

$$\mathcal{E} = \sum_{i=1}^{s} N_i \lambda_i; \quad \sum_{i=1}^{s} N_i = N. \tag{9}$$

Since the initial set of energies is "without preferences," i.e., is in general position, then all the multiplicities corresponding to (9) are equiprobable. The computer calculation time is related to the computer accuracy E_0 with respect to energy. The problem is how to determined N for which, at a particular instant of time, the computer cannot recover the initial data in view of the inaccuracy of the classical pattern or that of the quantum mechanical pattern (which is more accurate, but more cumbersome); the latter pattern, in turn, is not accurately described by an interaction of Lennard-Jones type.

Thus, we can draw the following conclusion. The initial data in the classical and quantum mechanical problems are forgotten because of external noise. As a result, the problem is reduced to the distribution $\{N_i\}$ (9). In this problem, we assume *a priori* that the initial data are forgotten and, therefore, so is the numbering of classical particles. Although the textbook [17] erroneously interprets the difference between the quantum mechanical pattern and the classical one, it, nevertheless, gives a valid interpretation of the numbering of identical balls. Therefore, we can take symmetric eigenfunctions for $\widehat{L}_N$.

Therefore, it only remains to obtain the distribution of the number of particles N_i using relations (9). If $s \gg N$, then (9) can be expressed as

$$E_0 \sum_{i=1}^{\infty} i N_i = \mathcal{E}; \qquad \sum_{i=1}^{\infty} N_i = N, \tag{10}$$

these relations coincide with those in the classical number-theoretic problem under the condition that $\mathcal{E}/E_0$ is integer, which, of course, is of no importance in the asymptotics as $s \to \infty$ and $N \to \infty$.

Thus, since the noise component has prevented us to recover the initial data and the number of particles N is preserved as well as the total energy $\mathcal{E}$, without given any preference[6] to any versions from (9), we assume all the variants satisfying the relation

$$\sum i N_i \leq \frac{\mathcal{E}}{E_0}, \quad \sum N_i = N, \tag{11}$$

to be equiprobable.

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[6]For a market model "without preference," see [16]

In this approach, we can also take into account the collision of billiard balls, the initial energy of all balls can only decrease due to friction and the passage of kinetic energy into thermal energy during collisions. The numb er of balls will remain the same and the total energy will not exceed the initial energy $\mathcal{E}$.

This approach can also be applied to turbulence if we consider such a significant invariant as the Kolmogorov spectrum.

Note another highly important difference between the statistical and dynamical approaches. If the experimenter presents some data, then, as a rule, this means that he has carried out many experiments and presented the data consistent with all the experiments. In addition, these data can be verified by other experimenters and only after that they will be universally accepted. This means that all the variants of relations (11) are, in a sense, equiprobable. If inequality (11) is replaced by the corresponding equality, then we obtain the well-known microcanonical distribution. But as shown in [22], the final results for the inequality and the equality coincide. Therefore, we have finally derived the well-known microcanonical distribution for the number of particles, whose permutation does not affect the counting result.

Thus the notion of different (distinguishable) particles is incorrect if one speaks about their density. From the point of view of density of the set of objects under consideration, these objects are indistinguishable, namely, any transportation of these objects does not influence the density. Therefore, one must not apply the Boltzmann distribution in thermodynamics. Since N is a large number and the value $\ln N$ is not large, one must use parastatistics (see [15], [18], [23] and formula (21) below).

So we arrived at some inconsistencies in the main laws of thermodynamics and statistical physics. One of the most important distinctions between them is that there is a positive chemical potential in the distribution for the "Bose gas" of finitely many particles N. Of course, this is related to the famous notion of Bose condensate. As was shown in [13], there exists a degeneracy temperature such that for $T = T_{\deg}$ the number of particles is maximal, $N_{\max}$, and if $N > N_{\max}$, then $N - N_{\max}$ of particles get into the Bose condensate with energy zero (or minimal). We present an example of such a condensate in number theory.

For this, we consider Koroviev–Fagot's trick, described by M. A. Bulgakov in the novel "Master and Margarita", which was already discussed in our preceding papers [23, 24]. In a variety show, he scattered n money bills of 1 tchervonets denomination among k spectators. We assume that all versions of scattering of n money bills over k spectators are equiprobable (the chaotic condition). This is equivalent to decomposition of an integer n into k terms. The logarithm of the number of possible versions $p_k(n)$ is the entropy. We consider two examples related to Fagot' trick.

Let n money bills be distributed over k_0 spectators, where k_0 is such that

$$p_{k_0}(n) = \sup_k p_k(n).$$

(Clearly, for $k = 1$ and $k = n$, the number of versions is equal to 1, and hence such a supremum exists.) Then, with a larger probability, k_0 spectators obtain a quantity of money bills. If for $k > k_0$, the number of versions and hence the entropy decrease, then the entropy is maximal when the remaining spectators do not get any bill, i.e., they get into the Bose condensate[7].

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[7]As follows from relation (11) known in this problem, this situation corresponds to the two-dimensional case and demonstrated the Bose condensate in the two-dimensional case with Remark 3 taken into account.

Now we assume that the number of spectators is $2k_0$. Then, roughly speaking, k_0 (i.e., a half) spectators obtain several money bills, and k_0 spectators do not obtain anything. Since k_0 spectators with a larger probability (see [15]) obtain zero of money bills, the number of versions of the distribution of money bills over spectators is also equal to $p_{k_0}(n)$.

We couple the spectators under the following condition: if somebody in a pair does not obtain any money bill, then the sum obtained by the other is divided, for example, in half. Therefore, we now have k_0 pairs, and the number of all versions is equal to the number of versions in the first example.

Therefore, the Kolmogorov complexity (entropy) in both examples is the same and equal to $\log_2 p_{k_0}(n)$, where k_0 is the number of pairs. Thus either case is equiprobable, i.e. it there were $2k_0$ spectators, then k_0 of them would not get anything and if the spectators coupled, then all the pairs would obtain some money bills, but the number of versions of the distribution still remains equal to $p_{k_0}(n)$, and none of the examples can be preferred. Both of the realizations is equiprobable. In other words, it may be that the spectators coupled, and it may be that k_0 spectators remain without any money bills.

If we speak about the social economic efficiency, then it would be better if the spectators coupled.

Thus, it is a priori unknown what is the results of the phase transition of an ideal Bose gas into condensate: pairs of particles or, as was previously assumed in physics, particles at the ground level. If we consider the repulsing potential, as N. N. Bogolyubov did in his famous work in 1947, then this problem remains unsolved. But if we consider the Lennard–Jones potential, then, as the author showed in [25], there are arising pairs. In this case, one significantly uses the Pontryagin–Andronov–Vitt theorem [26], which implies that the time of stay of a particle inside the barrier, which exists in the case of the Lennard–Jones potential, depends on the noise level or the gas temperature.

It is clear that the transition into the condensate state must occur with a larger probability, which a mathematician must estimate. These estimates were first performed in [15].

2 Problem of fluids

If some particles form pairs (dimers), then the free particles (monomers) occur in the fractal situation. This fractal dimension can in general be counted by the Hausdorff formula.

As is known, as the temperature increases, the number of dimers decreases, and hence the fractal dimension increases. And this means that one more pair of quantities must be introduced in thermodynamics: the extensive (dimension) quantity and the intensive quantity corresponding to it, which we call the "press". This can be done rather easily, because the thermodynamical potential Ω is known for parastatistics of any dimension. Its derivative with respect to the dimension is just the desired intensive quantity [13].

As for the problem shown in Fig. 1, it is clear that, for $E \leq E_{\min}$, there exist only monomers, and between $E_{\min}$ and $E_{\max}$, i.e., between the barrier bottom and height, there exist both monomers and dimers. Hence the fractal dimension between $E_{\min}$ and $E_{\max}$ is less than 3.

Let us consider the following natural variation of the notion of Bose condensate for the classical parastatistical gas. Since the parastatistical condensate results in the appearance of pairs (dimers), the number of free degrees of freedom increases, and hence one can speak
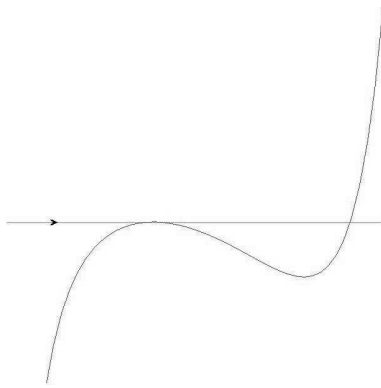
Figure 1: The trap for a fictitious particle in the system of the center of mass (SCM).

not about the energy disappearance in the parastatistical condensate but about the energy conservation by means of its redistribution. But if dimers, i.e., molecule associations, appear, then rotational and oscillatory components are added. This decreases the total energy of monomers, and hence $N_{\max}$ also decreases, which started an avalanche-like process until (with a larger probability) the translational energy of monomers disappears. And hence there is a phase transition in the energy redistribution and, naturally, a phase transition in the fractal dimension, which thus decreases.

We must not seek a phase transition of such a type in the domain, where the gas–liquid transition occurs according to the Van der Waals–Maxwell scheme, the scheme accepted by both the specialists in thermodynamics and the specialists in molecular physics of the old school. But the specialists in modern mathematical physics prefer to use the theory of percolation and renorm-group, as well as the possibilities due to computer computations.

The specialist in the theory of nucleation, especially experimenters, try to invent new theories and say that the classical theories are of no use anymore[8].

Both in the theory of percolation and in the theory of nucleation, as well as in the Van der Waals–Maxwell theory, an important role is played by the surface tension, treated as an additional energy. If this additional component is not considered, then the just described purely mathematical approach and the phase transition must be sought in the domain of critical temperature, i.e., in the domain, where the surface tension disappears. This structure, in which gas and liquid are indistinguishable, is called fluids from the time of alchemists.

Just as in Remark 2, we can write the microcanonical distribution, but under the condition that permutations in N_i are forbidden. As a result, we obtain a parastatistical distribution that is very close to the Bose distribution.

As was already noted, difficulties aries when the domains (2) are multiply connected. Moreover, a special case is the case of continuous spectrum.

As a rule, in physics in this case, the correct conditions of the Sommerfeld radiation are posed, which turn the problem into a not self-adjoint problem. If we go out into the complex domain through the cut, then it is reduced to the problem of finding Regge-type poles for a self-adjoint problem.

The mathematicians considered, as an example, a potential on a finite interval in the half-plane for the one-dimensional wave equation with a finite well and with the radiation

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[8]Cf. the opinion of the famous experimenters R. Strey and H. Reiss: "Present-day experiments in the homogeneous formation of droplets in argon display a dramatic discrepancy between the experimental data and the theoretical prediction based on the widely used old classical theory".

conditions on the boundary of the finite domain (the domain where the potential takes the values $[0, l]$).

Let l_1 be the value of x on the barrier maximum. But the "eigenfunctions" corresponding to the Regge poles (the poled of the resolvent continued through the cut into the complex domain) increase exponentially as $x \to \infty$. But the Regge "eigenfunctions" for which the real parts of the poles are close to the quasilevels of the well are sufficiently large in the domain of the well.

We prove that the solution of the Cauchy problem for the wave equation whose initial conditions are consistent with the radiation conditions (i.e., the derivative with respect to t depends on the initial function for $t = 0$) tends to zero at each point x of the support of the finite potential.

On the one hand, the passage to the semiclassics as $h \to 0$ simplifies the problem, on the other hand, there are two interacting parameters $h \to 0$ and $t \to \infty$.

In the problem under study, there is addition energy equal to the average energy $E_{\mathrm{av}} = kT$ (where k is the Boltzmann constant and T is the temperature) multiplied by the number of particles N (another large parameter).

Thus, we must compare the quantity h/t with NE_{av}. In fact, there is one more dissipation in gas, namely, the viscosity, which also cannot be neglected in mathematical computations and which ensures that the initial problem is not self-adjoint (the parameter corresponding to friction). The problem of determining the limit situation becomes significantly simpler in the language of nonstandard analysis. The rigorous theorems even in the case of this simplification are very c cumbersome. We present the main ideas.

In the semiclassical limit, one can assume that the well up to the barrier maximum and the domain from this point to the boundary condition are in no way related to each other. Only at the point E equal to the barrier maximum in infinite time, the classical particle can "creep" over the barrier (see Fig. 1).

The mathematicians consider the one-dimensional wave equation

$$h^2 \frac{\partial^2 \Psi}{\partial t^2} = h^2 \frac{\partial^2 \Psi}{\partial x^2} + u(x)\Psi$$

in the half-space $x \geq 0$, $u(x) = 0$ for $x > l$. The potential $u(x)$ has a smooth barrier with maximum at the point $x = l_1$. The stationary problem has the form

$$h^2 \frac{d^2 \varphi}{dx^2} + u(x)\varphi = k^2\varphi.$$

The radiation conditions outside the interval $[0, l]$ have the form const $e^{(-ikx)/h}$. The initial condition is

$$\Psi|_{t=0} = \Psi_0(x) \in L_2[0, l],$$

and $\Psi'|_{t=0}$ is chosen so that it correspond to the travelling wave outside the interval as $x \to \infty$. The residues at the Regge poles form a basis on this interval $[0, l]$.

Let Ξ be the linear span corresponding for $h \ll 1$ to all quasi-eigenfunctions whose eigenvalues are less than $E_{\max}$, and $P_{E_{\max}}$ is the projection on this subspace.

Let the initial function be equal to $\Psi(x) \in L_2[0, l]$. Then its part corresponding to the well is equal to $P_{E_{\max}}\Psi_0(x)$, and this part as $t \to \infty$ tends to zero in the interior of the domain of the well.

Now we consider the contrary problem, i.e., the "irradiation" problem. In other words, we pose conditions that are complex conjugate to the Sommerfeld conditions. This problem does not always has solutions. The well is being filled until

$$P_{E_{\max}}\Psi(x, t)\theta(x - l_1) = \Psi(x, t)\theta(x - l_1).$$

If
$$P_{E_{\max}}\Psi(x,t)\theta(x-l_1) \neq \Psi(x,t)\theta(x-l_1),$$
then the solutions do not exist, because the part
$$\left(1 - P_{E_{\max}}\right)\left[\Psi(x,t)\theta(x-l_1)\right]$$
reflects from the point $x = 0$, and the "irradiation" condition is not satisfied.

This phenomenon is similar to the following one. Assume that a negatively charged body is "irradiated" by positive ions. Then after a certain number of ions sticks to the body (fills the well) and neutralizes it, the other freely flying ions reflect from the body and the "irradiation" process stops. The conditions dual to the Sommerfeld condition are not satisfied any more, because the radiation process originates simultaneously. In our case, the role of attracting charges is played by Regge poles.

The Sommerfeld conditions are a specific case of the blackbody condition. This problem was posed even by Frank and von Mises in their survey as one of fundamental problems. The Feynman integral does not contain any measure, because it is impossible to pose the boundary conditions for the Feynman tube: the Feynman tube boundary is a black body. By definition, if the trajectory enters this boundary, it should not be considered any more,

In the Wiener integral of tunes, this is also a black body, but compared with the wave problem, the black body in the diffusion problem is understood as a situation in which the particles stick to the wall, and this means the zero boundary conditions for the heat conduction equation. After the transition to p-representations, as was shown in our work with A. M. Chebotarev [27], the zero boundary conditions give the Feynman tube in the p-representation, and it is possible to determine the measure for the finite potential.

The temporary energy capture in the laser illumination and its subsequent transformation into a directed beam also characterize the absorption-type trap of "irradiation" that further turns into radiation. Probably, the problem of black holes in astronomy is a problem of the same type. In the one-dimensional case, on a finite interval, the modern mathematical apparats can solve this problem completely. In this case, if $E_{\text{total}} = E_{\text{av}}N$, where N is the number of particles, then with a large probability) one can determine the number of particles inside the well and the number of particles outside it. By the way, this also readily follows from the concept of microcanonical distribution.

Indeed, the multiplicity (or the "cell" as it is called in [13]) of the eigenvalue E_{av} is different inside and outside the well: it depends on the density of eigenvalues as $h \to 0$ on a small interval $(E_{\text{av}} - \delta, E_{\text{av}})$. Obviously, this quantity is proportional to the width of each well on the interval $[0, l]$, i.e., to the length of $[0, l_1]$ and $[l_1, l]$.

Assume that N_1 is the number of particles in the well $[0, l_1]$, N_2 is the number of particles in the well $[l_1, l]$, d_1 is the length of the interval $[0, l_1]$, and d_2 is the length of the interval $[l_1, l]$. Then $(d_2/(d_1 + d_2))N$ of particles will reflect.

If $d_1 > d_2$, then the well–trap is not overfilled, and the irradiated particles remain in the well–trap. But if $d_2 > d_1$, then $(1 - d_2/(d_1 + d_2))N$ of particle fall out of the trap and reflect.

In numerous papers, the author has rigorously proved that there exists a parastatistical condensate similar to the Bose condensate in the one-dimensional and two-dimensional cases as well as in the case of fractal dimension greater than zero. This holds not only for identical objects (particles), but for objects (particles) that are assumed indistinguishable, such as those in the calculation of the "number" of teenagers, the "number" of women, the "number" of men, the "number" of money bills of one denomination, the "number" of

cites with population of over 1000 people, etc. This same applies when we speak about density. In the last case, the difference with thermodynamics is in only that there can be no finite thermodynamic limit (as stated in [28]), i.e., the ratio N/V, where N is the number of objects, and V is their volume, area, or length, may tend to infinity.

In this case, however, other small parameters that "neutralize" this convergence to infinity may exist; for example, as show in the previous paper [28], these may be nanodimensions (nanotubes).

In addition, the author proved that the parastatistical condensate, which is close to the Bose–Einstein condensate, does not necessarily lead to the accumulation of particles at the lowest energy level (roughly speaking, when they "stop"), but can lead to the formation of pairs of particles (dimes) and clusters and to the conservation of energy, i.e., passage of translational energy into rotational oscillatory energy.

In the present paper, we show that this point of view for the thermodynamics of imperfect gases in the interval of temperature variation from the critical temperature to the Boyle temperature is in good agreement with the experiment if for the interaction between the particles we consider the Lennard–Jones potential of the form

$$U(r) = 4\varepsilon\Big(\frac{a^{12}}{r^{12}} - \frac{a^6}{r^6}\Big), \tag{12}$$

where ε is the energy of the well depth and a is the effective radius. This agreement cannot be random.

The relations related to the microcanonical distribution do not take pairwise interaction into account. However, in the new axiomatics of the new ideal thermodynamics, we take into account the form of this interaction, namely, the Lennard–Jones potential, and the properties of this potential.

In the scattering problem with the Lennard–Jones potential, the pair energy is of the form

$$E = 4\varepsilon\Big(\frac{a^6}{r^6} - \frac{a^{12}}{r^{12}}\Big) \Big(\frac{\rho^2}{r^2} - 1\Big)^{-1}, \tag{13}$$

where ε is the depth of the well, a is the effective radius, and ρ is the impact parameter. Hence $r_0 = \Phi(E, \rho)$. By replacing

$$\frac{r}{a} = r' \qquad \frac{\rho}{a} = \widetilde{\rho}$$

we get rid of a.

For a given ρ, the minimum of r_1 and the maximum of r_2 on the graph in Fig. 1 are determined by the condition

$$\frac{dE}{dr} = 0. \tag{14}$$

At some point $\rho = \rho^0$, they coincide and, therefore,

$$\frac{d^2E}{dr^2} = 0 \tag{15}$$

at some point r^0. On the graph of $E(r)$ (Fig. 1) for $\rho = \rho_0$, the inflection points corresponds to $E = E_0$. In general, we associate the point ρ with the value $E_{\max}$, which is the maximal tangent to the well and with the minimal values $E_{\min}$. A pair of particles is "incident from infinity", i.e., from the point $r = \rho$, is tangent to the value $E_{\min}$, and slips into the well of depth $E_{\max} - E_{\min}$. Thus the actual well of scattering is turned over with

respect to the axis of the energy increase. This is related to the fact that the attracting part in the Lennard–Jones potential is negative. The calculation yields $E^0 = 0.8\varepsilon$. For $E > E^0$ the well (the trap) vanishes.

This criterion refers only to two colliding particles. The usual argument in molecular physics involves the symmetry of the average motion of the molecules in all six directions. Therefore, $1/12$ of all particles move toward one another. Since there are three axes, it follows that $1/4$ of all molecules collide.[9]. Their mean energy is

$$kT_{\mathrm{B}} = \frac{16}{5}\varepsilon,$$

where k is the Boltzmann constant. From physical considerations, the corresponding temperature, apparently, corresponds to the so-called Boyle temperature[10].

In Fig. 1, which describes the behavior of the mass center, the penetration beyond the barrier of particles moving from infinity and scattering at one another is only possible in the quantum case. However, in the presence of noise, such a penetration is also possible for classical particles by the Pontryagin–Andronov–Vitt theorem (see [31]). In our case, by assumption, all the variants of the microcanonical distribution are equiprobable. This condition yields significantly larger amplitudes of deviation in white noise. Therefore, we can assume that if the number of particles N exceeds some value of N_{cr}, then particles penetrate the barrier under the condition that the temperature is below T_{B} and transform into oscillating or rotating pairs.

Setting $\frac{r}{a} = x$, $\frac{\varrho}{a} = \widetilde{\rho}$, we obtain

$$E(x) = 4\varepsilon \left(\frac{1}{x^6} - \frac{1}{x^{12}} \right) \left(\frac{\widetilde{\rho}^2}{x^2} - 1 \right)^{-1}. \tag{16}$$

The derivative of the function $E(x)$ is

$$E'(x) = 8\varepsilon \frac{3x^8 - 2\rho^2 x^6 - 6x^2 + 5\widetilde{\rho}^2}{x^{11}(-\rho + x)^2(x + \rho)^2}.$$

After replacing $y = x^2$, the equation for the points of possible extremum is of the form

$$3y^4 - 2\rho^2 y^3 - 6y + 5\widetilde{\rho}^2 = 0.$$

Hence

$$\widetilde{\rho}^2 = 3y \frac{y^3 - 2}{2y^3 - 5},$$

and the dependence

$$E(y) = 4\varepsilon \left(\frac{1}{y^3} - \frac{1}{y^6} \right) \left(\frac{\rho^2}{y} - 1 \right)^{-1}$$

is of the form

$$E(y) = 4\varepsilon \left(\frac{1}{y^3} - \frac{1}{y^6} \right) \left(3\frac{y^3 - 2}{2y^3 - 5} - 1 \right)^{-1}. \tag{17}$$

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[9]The isotropy principle (of symmetry in all directions) is one of the key principles of molecular physics. It must also be formulated rigorously in mathematical terms as the isotropy principle in the theory of Kolmogorov turbulence or the Born–Karman conditions in the theory of crystals (the problem of the crystal volume finiteness problem), especially because of rapid development of the computer molecular dynamics similar to the computer anisotropic turbulence [29], [30].

[10]As we shall see below, the "well" is overfilled at a lower temperature.
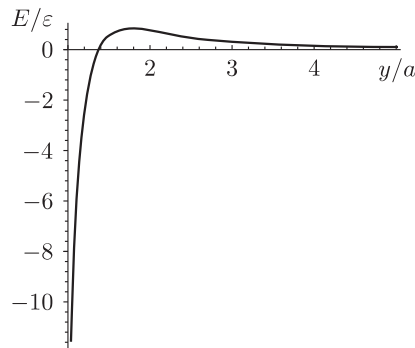
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Figure 2: The dependence of the energy E on y

The maximum value of $E_{max} = 0.8$ is attained at the point $y = \sqrt[3]{5}$.

The corresponding values of $\widetilde{\rho}$ are

$$\widetilde{\rho} = \frac{3}{\sqrt[3]{5}}. \qquad (18)$$

The graph of the function $E(y) = E$, where $E < 0$, has two points on the graph in Fig. 2 for $y = y_1(E) < \sqrt[3]{5}$ and for $y = y_2(E) > \sqrt[3]{5}$. These points correspond to the minimum and maximum of the trap in Fig. 1.

Note that the passage of a classical particle through the point y_2, when the energy of the particle corresponds to the point y_2 (see Fig. 2), is not a passage through an ordinary barrier. In passing from quantum mechanics to classical mechanics, we see that this point is no longer the usual turning point, and the classical particle, in the limit, penetrates into the well in infinitely large time.

In [32], we already discussed Koroviev's trick in a variety show when he scattered n money bills among k spectators and we shoed that if the number of spectators is twice as large as some critical number k_0, then, with a large probability, one-half of the spectators does not get a single bill. However, if they combine into pairs with a view to share the spoils, then most of them will get some bills with a large probability.

From the point of view of Kolmogorov complexity, both scenarios are equiprobable: none of them is preferable. As proved, given such a canonical distribution, there is also a critical number N_{cr}, as in the case of the Bose condensate.

By what has been said above, the axioms concerning the Bose distribution that $N - N_{cr}$ particles pass to the zero level (stop) are replaced by the following axiom: $N - N_{cr}$ particles form dimers, trimers, and other clusters that do not affect pressure and form Brownian particles in the gas[11].

The point E_{cr} for which the depth of the well (trap) is maximum is $E_{cr} = 0.286\varepsilon$. In our theory, this point corresponds to the critical temperature $T_{cr} = 4\frac{E_{cr}}{k}$, where k is the Boltzmann constant.

Let us present the table for $0.286\frac{\varepsilon}{k} = \frac{T_{cr}}{4}$ for different gases for which the formula for the gas is in correspondence with the depth 4ε of the well of the Lennard–Jones potential (not to be confused with the depth of a trap in the scattering problem).

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[11]Here the author tried to give a physical interpretation. In mathematical theorems of the author, the behavior of dimers and clusters is not considered as the behavior of physical objects. Only the fractal dimension is determined, as well as the partition of clusters into two classes.

Substance	ε, K	$T_{cr}/4$	$E_{cr} \cdot \varepsilon/k$
Ne	36.3	11	10.5
Ar	119.3	37	35
Kr	171	52	50
N_2	95,9	31	28
CH_4	148.2	47	43
C_2H_6	243.0	76	70
C_3H_8	242.0	92	70
C_4H_{10}	313.0	106	98
CO_2	213	76	52
AsH_3	281	93	82
GeH_4	237	77	59
H_2S	301	93	87
H_2Se	320	102	93
NH_3	300	101	87
PH_3	251.5	81	73
SiH_4	207.6	67	50

By our ideology, the dependence $\frac{E_{\min}}{E_{\max}}$ on $E_{\max}$, corresponds to an isochore under constant volume. The total energy equal to $E_{\max}$ corresponds to the temperature and $E_{\min}$ corresponds to the energy of the monomers. In view of the fact that, by our scheme, only the monomers exert chaotic pressure on the walls of the vessel,

$$4E_{\min} = \frac{PV}{R}$$

(the volume is measured in cm^3/mole).

Therefore,

$$\frac{4E_{\min}}{4E_{\max}} = \frac{PV}{RT} = Z,$$

where Z is the compressibility factor. The isochore $Z(P)$ is, indeed, the function $\frac{E_{\min}}{E_{\max}}(E_{\max})$.

We study the temperature range from T_{cr} to T_{Boyle}, i.e., the domain called *fluids* when the pressure exceeds P_{cr} and the surface tension making a liquid distinct from a gas, vanishes.

From the given table, we see that, for noble gases, the agreement is to within several degrees, while, for more complex molecules, it is to within 20 degrees on the Kelvin scale. Nevertheless, the percentage is not so large, because the difference of the temperatures, say, for water H_2O and nitrogen N_2 is as much as several hundred degrees.

Let us present a graph in Fig. 3 for several similar gases according to the law of corresponding states. We see that there is a rather good agreement only for the isotherms corresponding to the critical temperature, i.e., for $T_{\mathrm{r}} = \frac{T}{T_{\mathrm{cr}}}$, where T_{r} is the reduced temperature. The other isotherms give a mean discrepancy of 5%. Therefore, we can hope to obtain a better agreement for the first isotherm at $T = T_{\mathrm{cr}}$.

The principal thing for us is that the ideology involving parastatistical condensate and the formation of dimers, not of points located at the lowest level (as postulated in the case of the Bose gas) has been fully corroborated by experiments.

On the graph in Fig. 3, the critical point $E = 0.286\varepsilon$ corresponds to $Z = \frac{E_{\min}}{E_{\max}} = 0.444$. It is at this point that the avalanche process of parastatistical condensate originate and it is further strenthened, because the formation of dimers absorbs part of the energy,
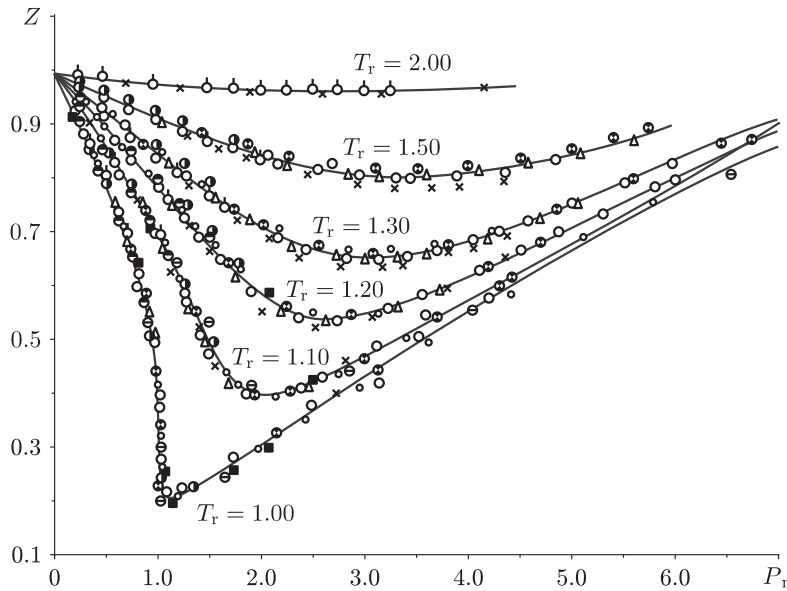
Figure 3: Experimental data for different values of $T_r = T/T_{cr}$ for different gases: ($\times$) — methane, ($\circ$) — ethylene, ($\triangle$) — ethane, ($\circlearrowleft$) — nitrogen, ($\blacksquare$) — isopental, ($\ominus$) — n-heptane. The other notation conventions: small circle — n-butane, vertically dashed circle — carbon dioxide, circle dashed on the right — water. The solid line corresponds to the data for hydrocarbonate.

enlarges the condensate and reaches the point at which all the monomers corresponding to E_{min} pass into rotating dimers.

This means that because the numbers of degrees of freedom of monomers is equal to 3 and of rotating dimes is equal to 2, it follows that this transition will occur up to the point $Z = \frac{2}{3}0.444$, equal to 0.296. In Wikipedia [33], the mean value for argon, krypton, nitrogen, carbon dioxide, and methane equal to 0.292 is given. As we see, this value is in good agreement with the graph in Fig. 3 and our concept of condensate and dimers.

But, according to our scheme, dimers not only rotate. There is also a small oscillatory component (the liquid is almost incompressible). As pressure increases, this component also vanishes and, further, the fluids behave as incompressible liquids and $Z(P)$ is a linear function.

The scattering problem for the Lennard–Jones potential divides the problem of the transformation of monomers into dimers into two areas. The first area belongs to the case in which the height of the barrier between the dimers and the monomers increases and is considered up to its maximal height. We say that this area of the scattering problem can be compared to the problem of occurrence of dimers in abstract thermodynamics[34].

As the barrier decreases with decreasing temperature, an additional energy barrier is needed to preserve the equilibrium "monomers–dimers". This follows from energy considerations. When we speak of "monomers" and "dimers", we have in mind a more general notion, because trimers and other clusters may form. In addition, dimers can be in translational motion, and thus contribute to the pressure on the walls.

We maintain that the equilibrium law well known in molecular physics for sufficiently low pressures and relate to the number of atoms in the molecule is violated in the sense of a greater role player by rotary and oscillatory components owing to the occurrence of molecule association. At the session of the Amsterdam Academy of Sciences in 1906, Van der Waals said that the violation of the equation of state discovered by him is due to the
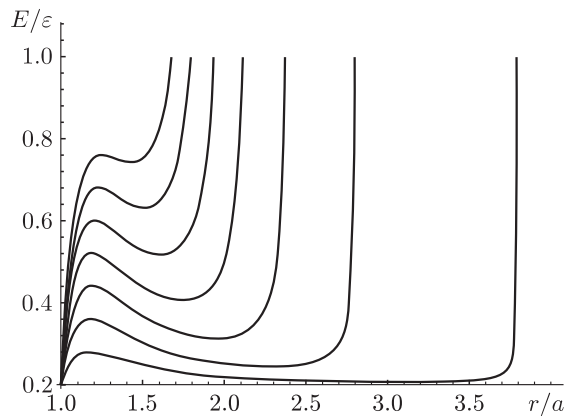
Figure 4: Wells and barriers in the scattering problem of two particles with Lennard–Jones interaction potential.

association of molecules. In modern language, the term "association of molecules" means the formation of dimers, trimers, and other clusters.

We divide the clusters into two forms: 1) those that contain at least one inner molecule (three-dimensional clusters) and 2) those that have no such molecule. The forme will be called "domains" by analogy with the corresponding mathematical term. Thus, domain are nanodrops, because they have molecules forming the surface of the domain. Among the gases noted in Fig. 2 in the first part of the papaer [35], there is carbon dioxide. In it, micelles, repulsive monomers, are formed as well. Thus, both dimers and micelles possess an additional barrier in the form of surface tension.

The part of the scattering problem corresponding to the decrease of the barrier with temperature in line with energy considerations involves the appearance of domains and micelles for the preservation of clusters and, therefore, another structure (not yet studied by us) must appear in abstract thermodynamics. We shall consider this situation in another paper. However, we can hardly expect that the study of that situation will lead to new discoveries in thermodynamics, possible only to the refinement of the equations of state due to Van der Waals and other scientists.

In the present paper, we speak about a new phase transition on the critical isotherm $T = 1$ and at the critical pressure $P = 1$. The volume V_{cr}/R undergoes a phase transition from the value $V_{\mathrm{cr}}/R = 0.444$ to the value $V_{\mathrm{cr}}/R = 0.296$. Here we deal with a phase transition of new type not discovered by physicists despite the fact that it can be observed on experimental graphs as a vertical segment (see Fig. 3 and 5). Nevertheless, the specialists in this area only say that this vertical line is a result of the inaccuracy of the experiment forgetting about the fact that in the ordinary Maxwell–Van der Waals phase transitions of the first kind, the exact experimental data do not fully agree with the theoretical calculations and the horizontal Maxwell segment cannot exist, because the Avogadro number is finite. This segment appears in theoretical constructions only in the asymptotic limit.

The phase transition $0.444 \to 0.296$ corresponds to the *law of redistribution of energies*; actually, this effect was discovered by the author in economics[12].

The role of the points $E_{\min}$ and $E_{\max}$ in the scattering problem (see Fig. 4) can easily be understood in terms of the general concept of the author regarding microcanonical

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[12]As I mentioned earlier, initially, I discovered a phase transition of this type while studying economics crises, and later tried to discover a similar effect in physics.

distributions constructed by the author. The scattering problem is considered in the phase space: (r, φ, θ) (the radius and two angles) are the coordinates and $(p_r, p_\varphi, p_\theta)$ are the momenta. It can be reduced to a two-dimensional problem in which (p_φ) is a free momentum. In addition, it has two invariants: energy and moment, and hence can be reduced to a one-dimensional problem. It is the points $E_{\max}$ [36] and the moment equal to $E_{\max}\rho^2(E_{\max})$, where ρ is the impact parameter corresponding to the maximum of the well.

The relationship with the general concept will be elucidated in detail in another paper. Here we present only arguments of physical nature.

The dimer can be formed in the classical domain if the scattering pair of particles has energy equal to the height of the barrier. This pair of particles penetrates into the well in "infinite" time and, due to the viscosity phenomenon and hence to a small loss of energy, gets stuck in it for a while; on the way back, this pair will hit the barrier as a result of the energy loss. But if the pari of particles passes above of the maximum of the barrier, then it is not known if there will be enough viscosity for this pair of particles to hit the barrier. Therefore, it is the sliding point that makes the main contribution[13].

Because of viscosity, the fictitious particle reaches the well bottom in a very large time, which means that only the rotational motion of the dimer remains. We have already mentioned the relaxation time influence, explaining the deviation from the theoretical values in the table of critical temperatures. Just in the same way, the relaxation time affects the oscillatory component. Therefore, it is natural that the greater the deviation of actual critical temperatures from their theoretical values, the lower the ground value of the phase transition, i.e., the larger the deviations from $Z = 0.296$ of the values given for the gases in the table.

Gas	Ne	Ar	Kr	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2	H_2S	H_2Se	NH_3	PH_3
$\frac{PV}{RT}$	0.307	0.292	0.291	0.292	0.290	0.288	0.278	0.273	0.274	0.283	0.293	0.242	0.275

The deviations of the data for propane C_3H_8, ammonia NH_3, and carbon dioxide CO_2 from the theoretical data are the largest in the table. Apparently, the ammonia and carbon dioxide to not reach the well bottom because of the polarity effect.

It follows from abstract thermodynamics that if the dimension of dimers and monomers is the same, the total energy inside and outside the well is also the same. Therefore, when we subtract the energy of dimers in the well it follows from the total energy of the monomers, as is seen from our general concept, that, for monomers, the energy remains equal to $E_{\min} = 1/4PV$. The physical thermodynamic relations imply that such a levelling-off occurs in infinite time. It is especially easy to see in the case of a plasma when it is easy to reproduce a pattern with a well and a barrier.

Since the point 0.444 corresponds to the fractal dimension 2.8, and the point 0.296 to the fractal dimension 2.45, using abstract thermodynamics [37], we can compare the corresponding values of $Z(P)$ for $P < 1$ with experimental curves in Fig. 3 and in Fig. 5. As Fig. 3 shows, experimental curves for different gases differ somewhat. In Fig. 6, we marked the values of the averaged isotherm $T = 1$ by black points.

In Fig. 5, we demonstrate the law of corresponding Van der Waals states and use the following notation: $T_r = \frac{T}{T_{\mathrm{cr}}}$, $P_r = \frac{P}{P_{\mathrm{cr}}}$. Then the dimensionless quantity, i.e., the

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[13]Since this pattern occurs in the negative energy half-plane, it is more correct to say 'below the maximum" instead of "above the maximum". The meaning is the same, but the picture is more illustrative.
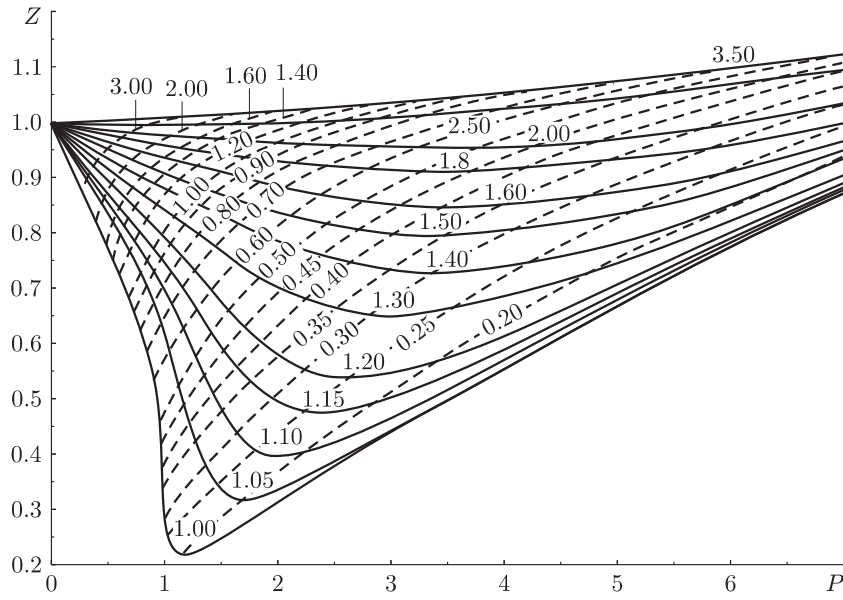
Figure 5: Experimental graph. $P = P_{\mathrm{atm}}/P_{\mathrm{cr}}$, $T_r = T/T_{\mathrm{cr}}$, T is the temperature in Kelvin degrees, V/R is the volume in cm^3/mole, R is the gas constant, and $Z = PV/(KT)$ is the compressibility factor. The isochores $V/R = \mathrm{const}$ are shown by dotted lines.

compressibility factor $Z = \frac{PV}{RT}$ becomes a dimensional quantity in the units cm^3/mole. To avoid this, we assume that the volume V is also dimensionless, taking the ratio $\frac{V}{R}$ cm^3/mole divided by unit volume equal to $1\,\mathrm{cm}^3$/mole in Fig. 5. This volume is shown in the figure by dotted line marked by 1.00. Then all the quantities are dimensionless, including the chemical potential. We assume that $\mu_{\mathrm{cr}} = T_{\mathrm{cr}}$ and $\mu_r = \frac{\mu}{\mu_{\mathrm{cr}}}$. In what follows, the subscript r is omitted.

First of all, we must find $Z(P)$.

To find the isotherm $T = T_{\mathrm{cr}} = 1$, we apply the well-known (in thermodynamics) general formula for $T = \mathrm{const}$, $d\mu = V dP$, V is the volume, P is the pressure, and μ it the dimensionless chemical potential.

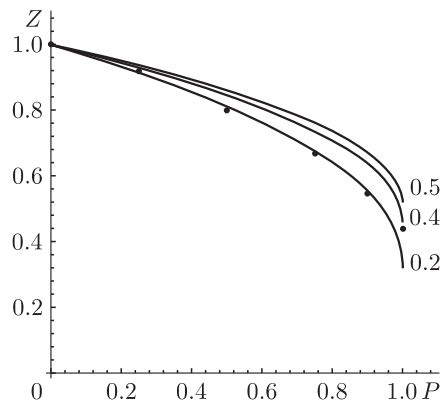Denote

$$y = e^{\mu}, \quad 0 \geq \mu > -\infty$$

Figure 6: Critical isotherm $Z(P)$ for dimensions 3 (curve 0.5), 2.8 (curve 0.4), and 2.4 (curve 0.2). Points correspond to the experimental isotherm.

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as $\mu \to -\infty$, $y \to 0$.

Then, for an ideal gas (see [23])

$$Z(y) = \frac{\Gamma(\gamma)}{\Gamma(\gamma+1)} \times \frac{\int_0^\infty \frac{\varepsilon^{\gamma+1} d\varepsilon}{e^\varepsilon - y}}{\int_0^\infty \frac{\varepsilon^\gamma d\varepsilon}{e^\varepsilon - y}}. \tag{19}$$

Therefore,

$$d\mu = d\ln y = Z(y)d\ln P,$$

and hence,

$$\frac{d\ln y}{Z(y)} = d\ln P, \quad y = y(P).$$

Denote $\ln P = \xi$, $\ln y = \mu$, $T \equiv 1$. Then

$$\frac{d\mu}{Z(\mu)} = d\xi, \qquad \xi = \int_0^\mu \frac{d\mu}{Z(\mu)}, \qquad P = e^{\int_0^\mu \frac{d\mu}{Z(\mu)}} = e^\xi \tag{20}$$

and $\mu = \mu(Z)$ according to formula (19).

As is known, in the kth-order parastatistics of fractal dimension γ, the distribution over energy has the form

$$Z_\gamma = \frac{\frac{1}{2m} \int_0^\infty p^{2+\gamma} \left\{ \frac{1}{e^{[(p^2/2m)-\mu]/\theta}-1} - \frac{k}{e^{[(p^2/2m)-\mu]k/\theta}-1} \right\} dp}{\int_0^\infty p^\gamma \left\{ \frac{1}{e^{[(p^2/2m)-\mu]/\theta}-1} - \frac{k}{e^{[(p^2/2m)-\mu]k/\theta}-1} \right\} dp}. \tag{21}$$

For the Bose-statistics, $k = \infty$, for the Fermi-statistics, $k = 1$. The parastatistics is characterized by a finite number k. In this case, the number of particles is assumed to be large. We associated this number k with the number of particles and obtain a new distribution: $k = N$ for $T < 1$ and $k = NT$ for $T > 1$. In our case, $k = N$, where N is the number of particles. Although $N \to \infty$, the chemical potential μ still can be positive and depend on N.

We consider the parastatic energy distribution for $k = N$ in the case where $\mu \geq 1$ and the dimension is equal to $2 + 2\gamma$ for $T = 1$

$$\int_0^\infty \varepsilon^{1+\gamma} \left\{ \frac{1}{e^{-\mu}e^\varepsilon - 1} - \frac{N}{e^{-\mu N}e^{\varepsilon N} - 1} \right\} d\varepsilon. \tag{22}$$

Near the point $\varepsilon = \mu$ we expand the expression in braces in a series up to $O\big((\varepsilon - \mu)N\big)^2$. We have

$$\frac{1}{(\varepsilon - \mu)\{1 + \frac{\varepsilon - \mu}{2}\}} - \frac{1}{(\varepsilon - \mu)\{1 + \frac{N(\varepsilon-\mu)}{2}\}} = \frac{1}{\varepsilon - \mu} - \frac{1}{2 + \varepsilon - \mu} - \frac{1}{\varepsilon - \mu} + \frac{N}{2 + (\varepsilon - \mu)N}$$

$$= \frac{N}{2 + (\varepsilon - \mu)N} - \frac{1}{2 + \varepsilon - \mu}.$$

For $\varepsilon = \mu$, this expression tends to infinity as $N/2$.

Both terms in braces in (22) tend to zero. Obviously, the integral

$$\int_{-a/N}^{a?n} \frac{N}{1 + xN} dx = \int_{-a/N}^{a/N} \frac{N\,dx}{1 + \xi} = \ln(1+\xi)\big|_{-a}^a = \ln(1+a) - \ln(1-a) = \ln\left(\frac{1+a}{1-a}\right) \tag{23}$$

is finite for $a < 1$.

At zero, the integrand exponentially tends to zero if $\gamma > -1$ is integrable as $\varepsilon \to \infty$. This implies that as $N \to \infty$, the expression in braces tends to $\delta(\varepsilon - \mu)$ and the integral in (22) tends to $\mu^{\gamma+1}$. This implies that

$$Z = \mu.$$

And since

$$d\mu = V dP = \frac{Z}{P} dP = \frac{\mu}{P} dP,$$

for $P > 1.5 P_{\mathrm{cr}}$, up to $1/\ln N$ (i.e., up to 4%), we obtain the diagonal line on the graph Z, P for the isotherm $T_{\mathrm{cr}} = 1$. This corresponds to the strict incompressibility of fluid as the pressure increases, which, as we see, coincides with experimental graph in Fig. 5. For $\mu = \frac{\alpha \ln N}{N}$ ($\alpha = \mathrm{const}$), the graph of the critical isotherm decreases and becomes the diagonal only for $\mu = \mathrm{const}$.

The press $\mathbb{P}$ is an intensive quantity dual to the fractal dimension γ for δ, $\mu > \delta > 0$, independent of N:

$$\mathbb{P} = \frac{\partial \Omega}{\partial \gamma} = -\frac{V}{\gamma + 1} \int_0^\infty \frac{\varepsilon^{\gamma+1}}{e^{(\varepsilon-\mu)/T} - 1} \Big(\ln \varepsilon - \frac{1}{\gamma + 1} \Big) d\varepsilon = \frac{VT}{\gamma + 1} \mu^{\gamma+1} \Big(\ln \mu - \frac{1}{\gamma + 1} \Big).$$

We note that the fluid critical volume at the phase transition instant, a jump in the fractal dimension, is equal to $V_{\mathrm{cr}} = 0.444$. This quantity is clearly determined. It also weakly depends on the repulsion degree of the Lennard–Jones potential. Therefore just this quantity is the main characteristics of the critical volume. As was already said, it is rather difficult to observe this quantity experimentally. It is much easier to observe the lower end of the vertical segment.

If the trajectory of rotation of a pair of molecules about the central point is nearly circular, then the energy redistribution from translational to rotational is $2/3 V_{\mathrm{cr}} = 0.296$. For noble gases, the trajectory ellipticity is rather small, and hence the energy redistribution is 0.292–0.290. But for carbon dioxide, it is more "elliptic", and hence the fall may attend the value 2.7, but the original critical volume remains 0.444.

The energy redistribution law results in the phase transition, see the vertical segment in Fig. 5. Further, the condensate is also formed as the fluid becomes incompressible in the end, the fractal dimension is then 2.4. Although distribution (21) is similar to the Bose distribution, the final condensate is an incompressible fluid consisting of clusters of dimension less than three, i.e., it does not contain domains or micelles.

At higher pressures, clusters, i.e., nuclei of crystals, appear. This fact also agrees with the author's general concept [37].

Note that, for gas dimers, the fractal dimension is equal to 2.8. As is readily seen from arguments in [13], if for the three-dimensional case, the Poisson adiabatic curve is $PV^{5/3} = \mathrm{const}$, then, for the dimension 2.8, the adiabatic curve will be $PV^{12/7} = \mathrm{const}$, and, for "liquid" fluids of dimension 2.4 the adiabatic curve is of the form $PV^{11/6} = \mathrm{const}$.

The averaged graph in Fig. 3 is of rather small accuracy, but this graph in dimension 2.8 is sufficiently well approximated with the same degree of accuracy.

The point is that the experiment even with argon is highly unstable bear the critical isotherm. Roughly speaking, it is considered as follows. A cylinder with a freely sliding piston on its upper cover is first fixed so that the volume is equal to the value of V_{cr} for argon $V/R = 0.3$ cm^3/mole. Here part of the argon is in liquid state and part of it in vapor state (see [38]). Further, the cylinder is heated up from $86\,K$ to $T = T_{\mathrm{cr}} \approx 159\,K$
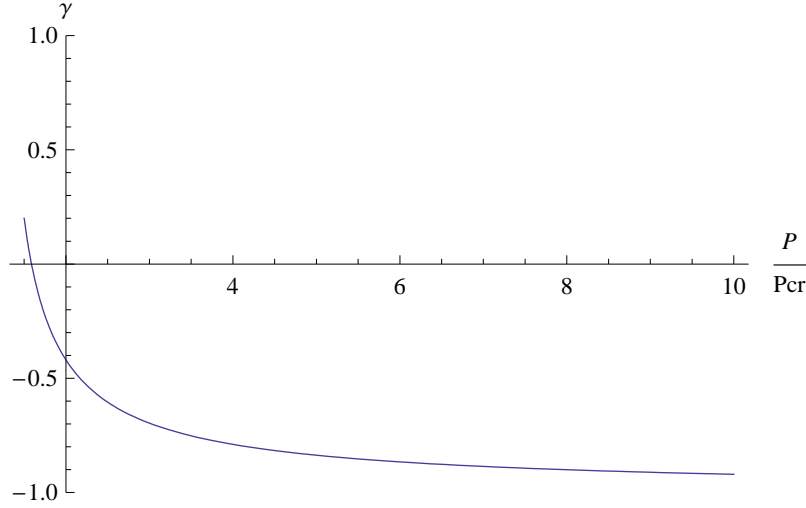
Figure 7: The graph of decreasing fractal dimension $2(\gamma + 1)$.

until the surface tension film disappears and a fluid is formed. So we obtain the lower point of the vertical segment in Fig. 5. Further, slowly releasing the piston and supplying heat so that the temperature remains equal to T_{cr} all the time, we must come to the point $P = 0.25 P_{\mathrm{cr}}$.

If, as the result of the experiment, the temperature drops below T_{cr}, then we have jumped to dimension 2.4, as is seen from the graph in Fig. 6. Therefore, here it is hard to abide by equilibrium thermodynamics, while theoretical calculations yield the dimension 2.8[14].

Essentially, after the redistribution of energies form the value 0.444 to the value 0.296, we come to a "liquid" fluid for all gases for which the experimental graph holds.

The incompressible part of the critical fluid is obtained for any dimension. And this variation in the dimension is a very important new phenomenon. The dimension reconstruction is a separate question. Apparently, this phenomenon explains the well-known "jamming" effect for glass (cf. [42]). Thus, although the volume does not vary with pressure, but, in this case, the dimers–clusters are "chewed" with a gradual reconstruction of clusters in the direction of a more strict (ideal) architecture. For the case of zero dimension and the architecture "self-organization", see [43].

The "chewing" effect, i.e., the dimension variation with P varying on the isotherm, occurs according to the law

$$\frac{d\gamma}{dP} = -\frac{\left[\frac{\partial \Omega}{\partial \mu}\right]_{\mu=P}}{\frac{\partial \Omega}{\partial \gamma}}, \qquad \Omega = -\int_0^\infty \varepsilon^\gamma \ln\left(1 - e^{(\mu-\varepsilon)/T}\right) d\varepsilon, \qquad \gamma|_{P=1.5P_{\mathrm{cr}}} = 0.2. \qquad (24)$$

The fractal dimension γ decreases (is "chewed") by the law (see Fig. 7)

$$\frac{d\gamma}{dP} = (\gamma + 1)\left(\ln P - \frac{1}{\gamma + 1}\right)^{-1}.$$

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[14]The author believes that if the temperature is raised slightly above T_{cr} at first, and then the volume is increased until the temperature drops to T_{cr}, then the dimension 2.8 in the experiment will be preserved. until $Z = 0.9$, and then becomes 3 in the phase transition of the second kind (see below).

As we known, $\gamma = 0.2$ corresponds to the fractal dimension 2.4. Thus, the fractal dimension has the form $2 + 2\gamma$, $\gamma > -2$. For $-1 < \gamma \leq 0$, the parastatistical term (21), where $k = N$, must be taken into account in Ω.

We described the critical isotherm $T = 1$. The process of passing to other isotherms is described in [40], [41] by successive steps of the T-mapping. In this paper, we do not consider this procedure, which requires a lot of computer computations.

We consider the isochore

$$\frac{E_{\min}}{E_{\max}}(E_{\min}). \tag{25}$$

for the scattering problem. For a fixed ρ, it means attraction, i.e., $|r_1 - r_2| < \rho$, where r_1 and r_2 are coordinates of two particles participating in scattering and denoted by the letter $r = r_1 - r_2$. Thus, this is the problem of "irradiation" by a flow of monomers. As was already mentioned, if $l_2 = \rho - l_1 < l_1$, where l_1 is the well width, then the monomers get stuck in the well, and if $l_2 = \rho - l_1 > l_1$, then a part of monomers return (i.e., are reflected).

In our case, the quantity $E_{\min}^{(1)}$ at this "transition point" is equal to 0.536, and $E_{\max}^{(1)} = 0.597$, and hence $Z \sim 0.9$. In Fig. 5, one can see that the isochore $V/R = 0.444 \text{cm}^3/\text{mole}$ lying above this point begins to stretch. This means that the isochore endures a phase transition of the second kind. This occurs due to variations in the dimension and, respectively, in the entropy [37]. This problem, just as the relation between the press and the pressure P, must be studied separately, because it is related to some generalization of the basic thermodynamical notions [35].

In the scattering problem, the volume is assumed to be equal to infinity. According to nonstandard analysis, infinities can be graded. In our case, we can consider the given isochore (Fig. (25)) on different scales, simultaneously extending or shortening both coordinate axes. It is only necessary to calculate the angle which they make with the isotherm $T_r = 1$. Let us carry out these calculations.

For the isochore

$$Z = \frac{E_{\min}}{E_{\max}}(E_{\min})$$

at the point $V/R = 0.444$, we can find the derivative at the point $E_{\max} = E_{\max}^{\text{cr}} = 0.286$.

We obtain

$$\frac{dZ(E_{\min})}{dE_{\min}}\Big|_{E_{\max}=E_{\max}^{\text{cr}}} = a = 1.951$$

On the other hand, $Z = \frac{PV}{RT}$ and, for $T_r = 1$,

$$\frac{dZ}{dE_{\min}} = \frac{dZ}{d(PV)}.$$

Hence

$$\frac{1}{a} = \frac{dPV}{dZ} = V\frac{dP}{dZ} + P\frac{dV}{dZ}$$

$$\frac{dV}{dZ}\Big|_{T=1} = \frac{1}{aP} - \frac{V}{P}\left(\frac{dZ(P)}{dP}\right)^{-1} = \frac{1}{aP} - \frac{Z}{P^2} \cdot \frac{1}{(dZ(P))/(dP)} =$$

$$\frac{1}{P}\left(\frac{1}{a} - \frac{Z}{P(dZ/dP)}\right) = \frac{1}{P}\left(\frac{1}{a} - \left(\frac{d\ln Z(P)}{d\ln P}\right)^{-1}\right).$$

The value of $Z(P)$ was already obtained above (19)–(20).

Theorem 2. *The fractal dimension γ does not vary along the isochore up to a point at which the trap width in the scattering problem for the interaction potential coincides with the distance from the barrier maximum point to the impact parameter ρ (Fig. 1).*

In our case, this coincidence occurs at the point $Z = \frac{0.536}{0.597} \sim 0.9$. We note that, for other Lennard–Jones potentials with a different degree of repulsion, the point of phase transition of the critical volume varies only in thousandth fractions. The value Z_{cr} at the critical point T_{cr}, P_{cr} is always equal to 0.44.

Thus, up to the value $Z = 0.9$, we can reconstruct the family of isochores, and hence of isotherms, because, at each point of the isochore, Z and P, and hence T, are determined.

Since in the three-dimensional case (the fractal dimension is 3) Z_{cr} for $\mu = 0$ is attained at the point $Z_{\mathrm{cr}} = 0.523$, and above the point $Z = 0.9$, the dimensions begin to increase up to the three-dimensional, i.e., if there are no dimers at the Boyle and higher temperatures, then, according to the above argument, the addition to the original number of particles–monomers is equal to

$$\alpha \frac{l_2 - l_1}{l_2 + l_1} \tag{26}$$

with a certain constant, which we determine by the condition: for $\mu = 0$, the dimension must be equal to 3, i.e., $\gamma = 1/2$. Hence $\alpha = \frac{0.523}{0.444} - 1 = 0.19$ for the Lennard-Jones type potential (12).

We find γ from the condition

$$Z_\gamma\big|_{T=1,\mu=0} = 0.444 + 0.19\frac{l_2 - l_1}{l_2 + l_1} \cdot 0.444.$$

Now, in our case, γ varies from 0.4 to 0.5 and depends on $E_{\min}$, i.e, on $\frac{PV}{4}$, where $V = 0.444$. But

$$-PV = T^{2+\gamma(PV)} \int_0^\infty \frac{\varepsilon^{1+\gamma}d\varepsilon}{e^{\varepsilon-\mu(T)} - 1},$$

where $\mu(T)$ is determined by the isochore $\frac{E_{\max}}{E_{\min}}(E_{\min})$ continued above the point $Z = 0.9$. Now we have determined the dependence $Z(P)$ for the new isochore whose dimension varies from 2.8 to 3 and the volume remains unchanged.

The quantity $l_2 - l_1$, as a function of temperature, increases almost exponentially approaching the Boyle temperature. To retain this fast increasing number of monomers in the volume 0.444, it is necessary to increase the pressure at the same rate. Therefore, the pressure increases much faster than Z, and this results in elongation of the isochore for $Z > 0.9$. The value of Z increases by 0.19 units and attains $Z = 1.19$, while the pressure increases more than twice.

The other isochores are similar to those constructed above, because their abscissas and ordinates increase and decreases by the same factors. The angle at which they intersect the critical isotherm $T = 1$ was calculated. To each point in the family of isochores there corresponds a pair of points $Z = \frac{PV}{RT}$ and P. Hence, for a given V, the temperature T is determined and the locus of points corresponding to the isotherm $T = \mathrm{const}$ is constructed.

In conclusion, I note that the rigorous proof of all the above statements is very cumbersome. It is based on the use of the correction to variations in the self-consistent field in the scattering problem and the complex germ method (in topology, the term "Maslov gerbe" is used, in mathematical physics, the term "complex germ"), as well as the ultrasecond quantization, where the operators of couple creation are used.

A more precise method of proof (the method of T-mappings) is given in [37], [41].

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